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The literature on polymer electrolytes is reviewed with emphasis on structural models, conductivity response in the microwave region, and the factors which influence both polymer-salt complex formation and ion transport in polyethers.

STRUCTURE AND ION TRANSPORT IN POLYMER-SALT COMPLEXES

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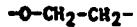
Polymer electrolytes based on alkali metal complexes of polyethers and cross-linked polyethers have significant cation mobility, which appears to arise from large-amplitude motions of the polymer. High chain flexibility not only promotes ion transport but it also is important for the initial formation of polymer-salt complexes. Several new polymer electrolyte systems are discussed which contain flexible polymer backbones and high concentrations of polar groups.

INTRODUCTION

The synthesis and characterization (1-4) of solvent-free alkali metal salt complexes of poly(ethylene oxide), PEO (I), prompted detailed electrical measurements with the thought that these materials might prove to be useful electrolytes for high energy density batteries (5,6). One potential advantage of polymer electrolytes is that they should conform to solid electrodes throughout charging and discharging cycles, and therefore facilitate the development of new high energy density solid state batteries. There are many fundamental aspects of polymer electrolytes which are ripe for investigation: the chemical variables which influence electrolyte formation, the relationships between structure of the polymer electrolytes and ion transport, and the detailed mechanisms for ion transport. This paper surveys accomplishments in the field of polymer electrolytes, with an emphasis on polymer-salt complex formation and ion transport mechanisms as revealed by the comparison of various response properties of the polymer electrolytes. This account will not cover any of the solvent swollen polymer electrolytes, such as traditional ion exchangers or solvent containing polymer membranes (7,8).

$$-O-CH_2-CH_2-$$

(I)
Poly(ethylene oxide)

POLYMER-SALT COMPLEX FORMATION

Simple ethers and short-chain polyethers are well known as solvents for alkali metal salts, and cyclic ethers (crown ethers) are effective complexing agents for alkali metal cations. Furthermore, complex formation between high molecular weight polyethers and alkali metal salts is known to occur in methanol solution (3). In all of these cases the dominant interaction is the coordination of ether oxygen atoms to alkali metal cations. The formation of solid polyether salt complexes fits well into this general pattern.

If we make the approximation that entropic factors, polymer reorganization energies, and residual cation-anion coulombic energies are constant for the formation of the various polymer salt complexes, for any given polyether and any given cation the formation of complexes should closely correlate with lattice energies of the alkali metal salts. As shown in Table 1, this type of correlation does have general validity, since complex formation is restricted to the salts of a particular cation which are below a threshold lattice energy. In keeping with this generalization, the lowest lattice energies and the highest propensities toward complex formation are found for alkali metal salts having large anions, such as I^-, ClO_4^-, and $SO_3CF_3^-$.

The stoichiometry of polymer-salt complex formation cannot be defined with the precision characteristic of the phase relationships for most simple inorganic systems. Nevertheless, an approximate limiting stoichiometry around 4 moles of polyether oxygen per mole of alkali metal salt is observed for many of the polymer-salt interactions (1,5,8). Recent research in our laboratory provides a number of examples in which higher salt concentrations are possible, such as $PEO\cdot3.5NaBH_4$. This higher salt concentration may arise from the partial filling of the coordination sphere of the Na^+ by tight ion pairing with the BH_4^- anion. Evidence for such ion pairing is available from both conductivity and spectroscopic measurements (9). By contrast, the $Na[B(C_6H_5)_4]$ complexes with PEO which we have prepared to date have on the order of 7:1 ratio of ether oxygens to alkali metal ion. Presumably, in this case the bulk of the counter ion, $B(C_6H_5)_4^-$, prohibits the formation of complexes with higher concentrations of salt.

Table 1. Comparison of PEO-Salt Complex Formation with Lattice Energies of the Pure Salts.[a,b]

	Li$^+$	Na$^+$	K$^+$	Rb$^+$	Cs$^+$
F$^-$	No 1036	No 923	No 821	No 785	No 740
Cl$^-$	Yes 853	No 786	No 715	No 689	No 659
CH$_3$COO$^-$	– 881	No 763	– 682	– 656	– (682)
NO$_3^-$	– 848	No 756	– 687	– 658	No 625
NO$_2^-$	– –	No 748	– 664	– 765	– (598)
Br$^-$	Yes 807	Yes 747	No 682	No 660	No 631
N$_3^-$	– 818	No 731	– 658	– 632	– 604
BH$_4^-$	– (778)	Yes (703)	– (665)	– (648)	– (628)
I$^-$	Yes 757	Yes 704	? 644	No 630	No 604
SCN$^-$	Yes 807	Yes 682	Yes 616	Yes 619	Yes 568
ClO$_4^-$	Yes 723	Yes 648	– 602	– 582	– 542
CF$_3$SO$_3^-$	Yes (<725)	Yes (<650)	Yes (<605)	Yes (<585)	Yes (<550)
BF$_4^-$	Yes (699)	Yes 619	– 631	– 605	– (556)
BPh$_4^-$	Yes (<700)	Yes (<630)	Yes (<630)	Yes (<600)	Yes (<550)

[a]No = no solvent free complex formed; Yes = solvent free complex formed; Values in parentheses are either theoretical or estimated lattice energies.

[b]Complex formation data is from reference (8) or the present work. Lattice energies are in kJ/mole from Jenkins, H.D.B. and Waddington, T.C., as quoted in The CRC Handbook of Chemistry and Physics, volume 61, Chemical Rubber Publishing Co., Cleveland Ohio, 1980-81.
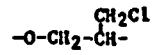
One attractive method for the preparation of complexes having the maximum salt concentration is the exposure of a polymer film to a saturated solution of the salt in a solvent in which the pure polymer and the complex are insoluble. This method will in principle lead to the thermodynamically stable polymer complex of maximum salt content, providing that the polymer is not swollen by the solvent and that the relaxation of the polymer chains is complete. Other methods for complex formation include the removal of solvent from a solution containing the polymer salt complex (1,5), and dissolving fine particles of the salt in the solid or the molten polymer.

As research on polymer electrolytes progresses toward more precise determinations of electrical properties, greater attention will have to be paid to the influence of impurities. Commercial polymers often contain significant concentrations of impurities, such as catalyst residues and water. For example, poly(ethylene oxide) contains several per cent of inorganic impurities, the majority of which can be removed by passage of an aqueous solution of the polymer through a mixed bed ion exchange column (10). In addition, the PEO salt complexes are hygroscopic, with the lithium salt complexes being particularly so. Water has been shown to have a large influence on the electrical properties of some lithium complexes (11), therefore systematic control and monitoring of water content is important. Infrared spectroscopic detection of the broad and intense water features around the 3,300 and 1,600 cm^{-1} regions provides a sensitive probe for the presence of adventitious water.
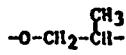
NEW POLYMER-SALT COMPLEXES

Poly(propylene oxide) and poly(epichlorohydrin) have received attention as host polymers for alkali metal salts. As with poly(ethylene oxide), all of these systems are based on a backbone of ether oxygens separated by two-carbon moieties (structures I, II, and III).

$$\begin{array}{cc} \text{CH}_2\text{Cl} & \text{CH}_3 \\ -\text{O}-\text{CH}_2-\text{CH}- & -\text{O}-\text{CH}_2-\text{CH}- \\ \text{(II)} & \text{(III)} \\ \text{Poly(epichlorohydrin)} & \text{Poly(propylene oxide)} \end{array}$$
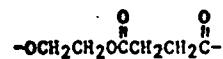
Samples of (III), which have been investigated in Armand's laboratory, and (II), which have been investigated in ours, were commercial atactic materials which produce amorphous complexes. Experiments with stereoregular analogues of these materials should provide useful clues to the steric factors which govern polymer-salt electrolyte formation. With the possible exception of poly(epichlorohydrin) the polyethers are attractive because they should exhibit a high degree of chemical inertness. The experimental situation with respect to the stability of the polyether electrolytes is unsettled. Armand observed a 4V stability range for PEO-Na[SO$_3$CF$_3$] (12) and he reported that the PEO·LiI electrolyte is stable to Li as judged by cyclic voltammetry (8), whereas Archer and Armstrong present some evidence for the formation of a resistive layer at the Li-

electrolyte interface (13). The exclusion and
monitoring of impurities such as N_2 (which
forms a nitride with Li) and H_2O will be par-
ticularly important in the determination of the
stability of these electrolytes.

A set of general polymer attributes which
should be conducive to polymer-salt complex
formation is presented here, slightly modified
from the original form (10): 1. The polymer
should have a high concentration of polar
groups, which will effectively solvate the
cation and/or anion. 2. The polymer backbone
should be highly flexible to permit polymer
reorganization and cation solvation. 3. In
general the polymer should have a low cohesive
energy density to produce a favorable free
energy change upon polymer-salt interaction.
Factors 2 and 3 are associated with properties
such as low glass transition temperatures, T_g,
and low melting points.

Potentially effective polar groups for polymer
electrolytes are suggested by the functional
groups found in polar organic solvents such as
sulfones, sulfoxides, nitriles, esters, amides,
amines, imines, ketones, and sulfides. Unfor-
tunately most of these groups are more electro-
chemically active than ether linkages. Initial
results from studies in our laboratory on new
host materials containing some of these polar
groups have produced encouraging indications
that many new polymer electrolytes may be pre-
pared. The most thoroughly studied new polymer
host is poly(ethylene succinate), IV, which has
been found to form complexes with Li[BF_4],
Li[CF_3CO_2], Li[SO_3CF_3], and Na[SO_3CF_3].

$$-OCH_2CH_2O\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}-$$

(IV)

Poly(ethylene succinate)

Complexes having 2:1 polymer repeat units per
formula unit of salt have been prepared and
there are good indications that higher salt
concentrations can be achieved. Conductivities
on the order of 1.3×10^{-7} ohm^{-1} cm^{-1} were
obtained for the Li[BF_4] salt at 41°C. A quite
different series of complexes was prepared from
poly(ethylene sulfide), V, or poly(propylene
sulfide), VI, with silver salts such as Ag[NO_3]
and Ag[SO_3CF_3]. The 5:1 poly(ethylene sulfide)-
Ag[SO_3CF_3] complex displayed a conductivity of
about 4.6×10^{-7} ohm^{-1} cm^{-1} at 65°C.

$$-SCH_2CH_2- \qquad -SCH_2CH_2CH_2-$$

(V)   (VI)

Poly(ethylene sulfide)   Poly(propylene sulfide)

An interesting new approach to polymeric con-
ductors is the use of cross-linked networks of
low molecular weight poly(ethylene oxide) into
which a salt is introduced (14,15). The intent
with these materials is to achieve a combination
of good mechanical and electrical properties.

STRUCTURE OF POLYETHER SALT COMPLEXES

The structures of pure poly(ethylene oxide) and
of a $HgCl_2$-PEO complex are known from X-ray
structure determinations combined with vibra-
tional spectroscopy (16,17). The pure polymer
consists of an extended helix, having a fiber
repeat distance of 19.48 Å, and the mercuric
chloride complex consists of a zigzag polymer
backbone with oxygen atoms coordinated to mer-
cury. A similarly detailed X-ray analysis of
the alkali metal salt complexes of PEO has not
been carried out. In their original work on
the PEO complex with KSCN, Fenton, Parker, and
Wright determined an X-ray fiber repeat dis-
tance of 8.1 Å (1). More recent detailed infra-
red and Raman spectroscopic data have revealed
several structural features (10). Mid-infrared
data indicate that the OCH_2-CH_2O moieties
assume a gauche conformation. Raman data in a
similar frequency range provide evidence for a
symmetrical breathing mode characteristic of
O_n-Na stretching motion, and the far-infrared
displays bands which are characteristic of
translational modes for alkali metal ions in a
solvent cage. Significantly, these latter
features scale approximately as the square root
of the mass of the alkali metal ion and are
independent of the nature of most anions. A
structural model which is consistent with these
vibrational data and the X-ray fiber repeat
distance is a sequence of trans(CC-OC),
trans(CO-CC), gauche(OC-CO), trans(CC-OC),
trans(CO-CC), and gauche-minus(OC-CO) confor-
mations. This results in a helical configura-
tion having an interior channel lined with
ether oxygen atoms, and large enough to accom-
modate a K$^+$ ion (10). A view down this helical
tunnel is given in Figure 1. The anions appear
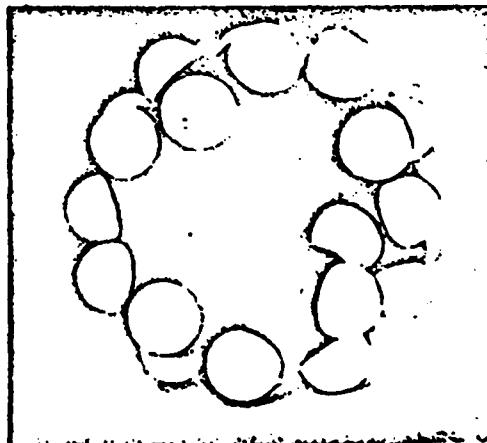
Figure 1. View down the axis of the proposed
helical configuration for the PEO backbone in
its complexes with sodium salts.

to lie outside the helix, with no direct cation-anion contact in most cases. The lack off crystallinity for the rubidium and cesium salt complexes is consistent with this model because the helical channel is too small to accommodate these cations.

A double helix of intertwined PEO chains has been proposed to accommodate recent estimates of the unit cell dimensions for PEO·NaSCN obtained from X-ray diffraction on oriented polycrystalline material (18). This particular model, however, places some of the OCH$_2$-CH$_2$O groups in a nearly eclipsed configuration which would suffer from unfavorable repulsion of non-bonded atoms. The structures of polymers are always difficult to determine and these complex systems are particularly so.

CONDUCTIVITY AND ION TRANSPORT MECHANISMS

Transference number measurements at 23.5°C for PEO·NaSCN demonstrate that t(Na$^+$) is very close to 1.0 (19), and unpublished NMR results indicate that t(Li$^+$) > 0.95 for a polyether lithium electrolyte (8). In addition, a variety of evidence indicates that anions have finite but very small mobilities in these materials. For example, complexes can be formed from solid salt plus solid polymer and conversely a second, salt phase can be observed to form below the melting range of some salt-rich complexes.

The simplest temperature dependent conductivities are exhibited by highly crystalline complexes such as those between sodium salts and PEO. The early reports on these materials gave two linear segments in the log σ vs 1/T plots (2,20). Recently independent research in two laboratories has demonstrated that the two-slope behavior disappears when the conductivity experiments are performed on fully complexed materials (9,18). The break observed in the original reports on the low salt materials is close to the melting temperature range of PEO, and the interpretation which we prefer is that this break is associated with the melting of residual pure or lightly doped PEO.

The non-crystalline polymer electrolytes such as those of poly(propylene oxide) alkali metal salts or PEO with rubidium or cesium salts, display curved log σ vs 1/T behavior (21). The empirical Vogel-Tamman-Fulcher equation, 1, which describes transport properties in viscous media, appears to fit the temperature dependence of the ionic conductivity very well (21).

$$\sigma = \frac{A}{\sqrt{T}} \, exp\left(\frac{-B}{T-T_0}\right) \qquad (1)$$

In this equation A, B, and T$_o$ are empirical constants, with T$_o$ corresponding fairly closely to the glass transition temperature, T$_g$, of the polymer complex. This functional dependence may be described by a model in which motion of the polymer chain is crucial for the ion transport

process. From energetic considerations it appears most likely that the cation moves without breaking many cation-oxygen interactions (22). Thus large amplitude polymer segment motions coupled with the breaking and making of one or possibly two cation-oxygen interactions per cation provides a means of cation transport which is quite unlike the hopping mechanism commonly observed for simple inorganic electrolytes. The importance of the glass transition temperature, and therefore the polymer segmental motion, has been demonstrated experimentally for the polyurethane-type polyether network complexes (23), for which the glass transition temperature can be varied widely. There is a clear indication that a fruitful approach to increased ion mobility in polymer electrolytes is to seek systems in which T$_g$ is as low as possible.

Even though linear log σ vs 1/T plots are obtained for crystalline polymer complexes, such as PEO with lithium, sodium, and potassium salts, it appears likely that polymer motions are strongly coupled to the ion transport process in these materials as well. Microwave measurements indicate that the highly crystalline complexes exhibit strong conductive response in the GHz region which is comparable to that of pure PEO (24) and this response is attributed to high frequency segmental motion of the polymer backbone. Below 1 MHz the ion containing polymer has much higher conductivity than the pure polymer, Figure 2. This observation affords evidence that in the crystalline PEO salt complexes the low frequency ion motion is assisted by higher frequency polymer motion.
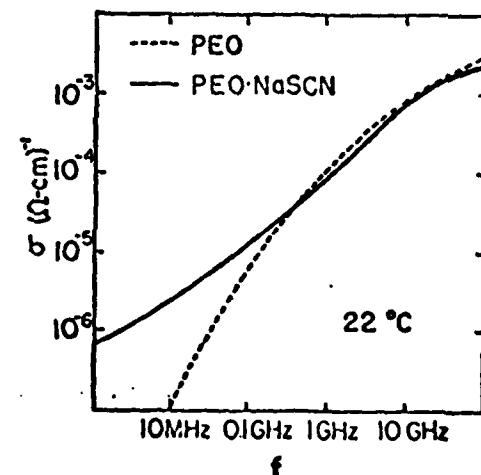

Figure 2. Variable frequency conductivity of pure PEO --- and 4.5PEO·NaSCN ——.

One oustanding problem is the effect of polymer orientation on conductivity. As yet there have been no reports of systematic conductivity measurements on oriented polymer electrolytes. Our understanding of the ion transport mechanisms also would be improved by information on the volume of activation for ion transport, which will require the measurement of conductivities under hydrostatic pressures. Some pressure dependent polymer electrolyte conductivity data have been reported under nonhydrostatic conditions (25).

CONCLUSIONS

The field of polymer electrolytes has developed rapidly. Quantitative microscopic theories for ion transport mechanisms in these materials are not yet available, but some qualitative concepts with predictive value have emerged. Of the currently known systems, perHaps the most promising for room temperature battery electrolytes are the lightly cross-linked polyethers, for which the required low T_g can be fairly readily attained.. It was recently estimated that a polyethem with $T_g = -80°C$ should display a conductivity in the 10^{-3} to 10^{-4} range at room temperature (23). This is sufficiently high to offer considerable incentive for further research on these materials.

ACKNOWLEDGEMENTS

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